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Propulsion Research
Propellant Chemistry Investigation
SEMIANNUAL TECHNICAL REPORT

(1 July - 31 December 1962)

28 FEBRUARY 1963

Prepared by L. SCHIELER
Aerodynamics and Propulsion Research Laboratory

Prepared for COMMANDER SPACE SYSTEMS DIVISION
UNITED STATES AIR FORCE
Inglewood, California



LABORATORIES DIVISION • AEROSPACE CORPORATION
CONTRACT NO. AF 04(695)-169

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SSD-TDR-63-34
Part I

Report No.
TDR-169(3210-10)TR-2
Part I

PROPELLANT CHEMISTRY INVESTIGATION

SEMIANNUAL TECHNICAL REPORT
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Prepared by
L. Schieler
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El Segundo, California

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ABSTRACT

Continued chemical research on high-energy propellants was accomplished on various aspects of the propulsion research program to support the overall objectives of SSD. In one study, it was found that the extent of chemical reaction between $TiCl_4$ and atomic hydrogen is pressure-dependent, with greater reaction occurring at lower pressures. At a pressure of 8 mm, formation of $TiCl_2H_2$ and $TiClH_3$ was observed, while at 4 mm pressure, TiH_4 and $TiClH_3$ were formed. In another study, classical methods of synthesis are being used in an attempt to produce metal hydrides. During this reporting period, various fractions of the reaction products were purified for study of the elemental composition and molecular structure. In the continued study to provide a stable salt of SF_5^{-1} , it was concluded that the previously-prepared salt of SF_5^{-1} , or $(CH_3)_4NSF_5$, is thermally stable. In the study of fluorocarbons as possible solid propellant binders, further investigation was conducted on the reactions previously reported, i.e., the telomerizing of 1,1,2,8-tetrahydropentafluorooctene by hydrogen peroxide in certain oxygenated solvents to form fluorine-containing telomers bearing hydroxyl and carbonyl groups. Telomerization of perfluoroheptene-1 is being investigated. In still another phase of the program, the previously-reported reaction between anthrone and thionyl chloride was more thoroughly studied.

Classified portions of this chemical propellant research are presented as Part II of this report, under separate cover.

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I. INTRODUCTION

During the period of 1 July 1962 to 31 December 1962, experimental and theoretical investigations were continued on a propellant chemistry research program to furnish the background information necessary for technical support of Air Force Space System Division objectives. In terms of propulsion problems, Space System Division objectives depend on the availability of large boosters capable of placing large payloads into orbit, propulsion suitable for in-space maneuvering, high-energy space storable propellants, and means of accurately detecting radiation from rocket exhaust gases.

In support of these general objectives, the propellant chemistry research program has emphasized 1) investigation of high-energy propellant ingredients such as metal hydrides and fluorine compounds, 2) synthesis of new solid propellant resin binders, 3) catalytic decomposition of hydrazine, 4) investigation of advanced organic synthesis reactions, 5) completion of a comprehensive propellant performance calculation program, and 6) measurement of the ultraviolet radiation characteristics of propellant exhaust gases.

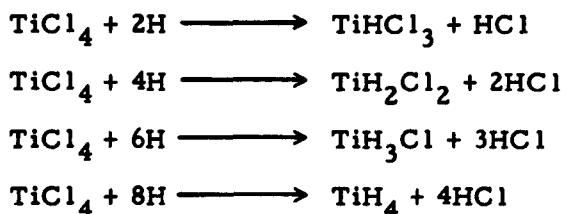
The unclassified aspects of the propellant chemistry research program will be presented as Part I of the report. Classified aspects will be presented as Part II, under separate cover.

II. DISCUSSION

A. REACTIONS BETWEEN $TiCl_4$ AND HYDROGEN

Due to the importance of metal hydrides in the chemical formulation of high energy propellants, determination of the maximum number of stable bonds which various metals are capable of forming with hydrogen is considered to be advantageous to future developmental efforts. As part of a continuing program to make these determinations, the products of a reaction between gaseous titanium tetrachloride ($TiCl_4$) and atomic hydrogen were studied by use of a mass spectrometer. The laboratory apparatus and techniques used in this study have been described in previous reports (Ref. 1 and 2).

Titanium tetrachloride was selected as the reactant for the initial study to support the possibility that hydrides of titanium which contain more hydrogen atoms than are present in the known dihydride of the metal (TiH_2) might be capable of stable existence. The existence of TiH_4 has long been postulated, as the titanium atom has four valence electrons in the ground state. It was hoped that the following substitution reactions would occur:



Reactions between $TiCl_4$ and atomic hydrogen were carried out at total reactant pressures of 29.5 mm, 8 mm, and 4 mm. In each case, the reactant mixtures consisted of 10% $TiCl_4$ and 90% H_2 . Mass spectra were taken of each reactant mixture prior to the generation of atomic hydrogen by mercury photosensitization. The atomic hydrogen was produced by ultraviolet irradiation of the mercury vapor through the following reaction sequence:



Verification of reaction between TiCl_4 and atomic hydrogen was obtained by comparison of the mass spectra taken before and after irradiation.

The relative extent of reaction at the three levels of pressure can be deduced from the data in Table 1 which gives the decrease in intensity of the mass peak 188. The mass peak was attributed principally to $\text{Ti}^{48}\text{Cl}_4^{35+}$ which is the parent ion of $\text{Ti}^{48}\text{Cl}_4^{35}$. It can be seen that the reaction at 29.5 mm was slight by comparison with that at lower pressures.

Table 1. Relative Reaction of TiCl_4 and H_2 at Varied Pressures

Pressure, mm	Percentage Decrease in Mass Peak 188 ($\text{Ti}^{48}\text{Cl}_4^{35+}$)
29.5	17
8.0	74
4.0	70

The data in Table 1 provide only an indication of the amount of TiCl_4 reacted. The products formed were determined from an analysis of the other mass peaks observed.

There are five isotopes of titanium and two of chlorine (Table 2). From these data it can be predicted that principal ion peaks for TiCl_4 should appear at mass spectrum (m/e) values in the regions of 46-50, 81-87, 116-124, 151-161 and 186-198, corresponding to various isotopes of the fragments Ti^+ , TiCl^+ , TiCl_2^+ , TiCl_3^+ and TiCl_4^+ . However, because of the isotope abundance values, the principal mass peaks for these species should be at 48, 83, 118, 153 and 188, respectively. Moreover, if TiCl_4 were converted to hydrides of the type TiCl_3H , TiCl_2H_2 , TiClH_3 and TiH_4 ,

substantial increases in the intensities of the mass peaks at 154, 120, 86 and 52 should be observed. Accordingly, the ratios of mass peaks at 52/48, 86/83, 120/118, and 154/153 should be examined before and after irradiation to detect the formation of these higher hydrides and chlorohydrides of titanium.

Table 2. Isotopes of Titanium and Chlorine

Isotope	Abundance, %
Ti ⁴⁶	8.0
Ti ⁴⁷	7.4
Ti ⁴⁸	73.8
Ti ⁴⁹	5.5
Ti ⁵⁰	5.3
Cl ³⁵	75.5
Cl ³⁷	24.5

At a pressure of 29.5 mm, no substantial difference in the mass peak ratios was observed through measurements taken before and after irradiation as the reaction between $TiCl_4$ and atomic hydrogen was relatively slight. However, at a pressure of 8 mm, the ratio of the mass peaks at 120/118 increased from 0.21 to 0.47 upon irradiation. Also, the ratio of mass peaks at 86/83 increased from 0.05 to 0.45. These data clearly demonstrate that the large-scale reaction denoted by data in Table 1 results in the formation of $TiCl_2H_2$ and $TiClH_3$. There was no evidence for TiH_4 formation at 8 mm.

At a pressure of 4 mm, the mass ratios at 86/83 were again observed to rise from 0.05 to 0.47 upon irradiation, indicating the formation of $TiClH_3$. In addition, the mass ratios at 52/48 rose from 0 to 0.16, demonstrating

that TiH_4 had been formed. There was an additional increase in the mass ratios at 51/48, 50/48 and 49/48, indicating the presence of the ions TiH_3^+ , TiH_2^+ and TiH^+ ; the respective increases were 0 to 0.21, 0.06 to 0.21, and 0.14 to 0.40. It is not known whether TiH_3^+ , TiH_2^+ and TiH^+ are indicative of the isolated existence of TiH_3 , TiH_2 and TiH among the reaction products, or whether these species are fragmentation products from TiH_4 .

To summarize, the extent of reaction between TiCl_4 and H is pressure-dependent, and reaction is slight at higher pressures. At a pressure of 8 mm, TiCl_2H_2 and TiClH_3 were observed to form, while, at a pressure of 4 mm, the substitution of hydrogen for chlorine in TiCl_4 is more complete and formation of TiH_4 and TiClH_3 was observed. Also observed (at 4 mm) were the ions TiH_3^+ , TiH_2^+ and TiH^+ which may have been derived from the fragmentation of TiH_4 , rather than being indicative of the presence of TiH_3 , TiH_2 and TiH .

B. METAL HYDRIDE SYNTHESIS

In addition to preparing metal hydrides by the reaction of atomic hydrogen with metal-containing compounds, classical methods of synthesis are also being investigated.

The existence of binary stoichiometric transition metal hydrides has been the subject of considerable controversy since Weichselfelder (Ref. 3) first claimed the synthesis of such compounds by classical techniques. It has been reported that Weichselfelder's observations had been substantiated (Ref. 2); however, this was only in regard to the active hydrogen content of the complex reaction mixture. While the H to Fe ratio was found to be close to 6:1, other elements were present in the reaction mixture, and it was not at all obvious that FeH_6 was present as claimed by Weichselfelder. In the previous report (Ref. 2), the separation of the complex reaction mixture into crude fractions based on solubility in diethyl ether, tetrahydrofuran (THF), and pyridine was reported. The fractionation procedure and fraction

designations are presented in Fig. 1. During the present reporting period, further characterization of the reaction products was accomplished.

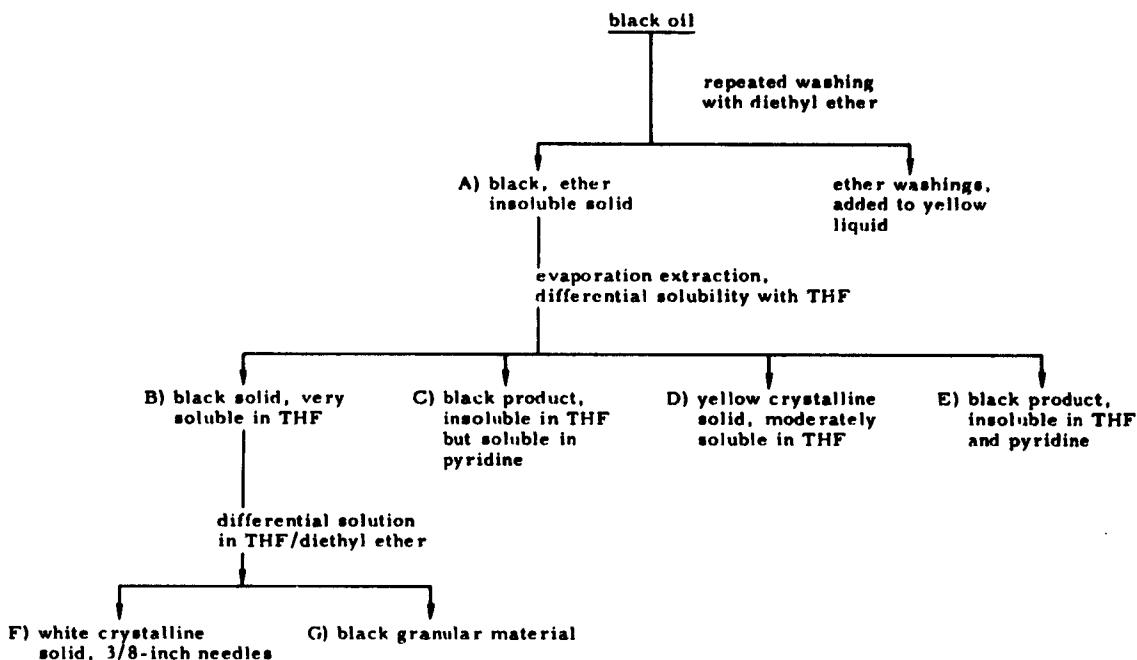


Fig. 1. Separation of Reaction Products

- The original ether-soluble supernatant contained only about five percent of the original Fe present in FeCl_3 ; there was approximately 17 times as much magnesium as iron in this fraction. Yet 20 to 30 percent of the total active hydrogen was present in this original supernatant, strongly indicating that the hydrogen is not primarily bonded to iron. Very significantly, it was found that fractions C and G (Fig. 1) are ferromagnetic. Streamers of C diffusing into pyridine were observed to be deflected by a magnet. Even solutions of G in tetrahydrofuran (THF) are ferromagnetic, the meniscus of

the solution following the movement of a magnet. Both the C and G fractions were colloidal in nature and exhibited a marked Tyndall effect. Quantitatively, fraction G is very much larger than C. It is estimated that about 90 percent of the original Fe was distributed between fractions G and E. Whereas E was insoluble in all solvents tried, G formed a colloidal solution in THF. That colloidal solutions of iron are ferromagnetic has been previously demonstrated.

The various fractions have been purified to the extent that it is now possible to initiate investigation of the elemental composition and molecular structure of the primary products of the reaction.

C. STABLE SALTS OF SF_5^{-1} ANION

To date, considerable effort has been devoted to preparation of stable salts of the SF_5^{-1} anion. Sulfur in this electronic state, in which both the oxidation state and coordination number are five, was unknown before the present investigation. From the viewpoint of solid composite propellants, sulfur in this electronic configuration could be very desirable if high energy ligands such as OF or NF_2 were substituted for F. Efforts have been directed toward preparing a stable salt of SF_5^{-1} because the simple fluoride is the most likely anion of this type to be capable of stable existence. Previous reports have indicated that the SF_5^{-1} anion cannot be prepared in salts containing simple metal cations or with bulky complex cations (Ref. 2 and 4). However, $(CH_3)_4N^+SF_5^{-1}$ has been prepared and partially characterized (Ref. 2). Final characterization of the latter is described in the present report.

Previous anomalous behavior in the stoichiometry of formation of $(CH_3)_4NSF_5$ from $(CH_3)_4NF + SF_4$ was explained when samples of $(CH_3)_4NF$, free of bifluoride impurity [$(CH_3)_4NHF_2$], were reacted with SF_4 . It was shown that the bifluoride, which does not react with SF_4 , largely accounts for the apparent lack of stoichiometry in the 1:1 reaction between $(CH_3)_4NF$ and SF_4 . A stoichiometry closely approaching unity occurs when bifluoride is largely absent from $(CH_3)_4NF$.

It was also demonstrated that $(\text{CH}_3)_4\text{NSF}_5$ does not decompose continuously at room temperature, but rather exhibits the equilibrium decomposition pressure characteristic of SF_4 . At 25°C this equilibrium pressure is 2 to 3 mm; the latter is maintained for at least two days. At 60°C the comparable decomposition pressure is 19 mm. On this basis, the $(\text{CH}_3)_4\text{N}$ salt of SF_5^{-1} is thermally quite stable.

D. SOLID-PROPELLANT BINDERS

The properties of high thermal stability and high specific impulse in reaction with metals and hydrides make fluorocarbons attractive as solid-propellant binders. In order to be able to incorporate such binders in solid motors, the formation of the binder in-situ from liquid pre-polymers would be advantageous. Toward this end, a program is underway to explore the formation of fluorocarbon telomers bearing functional groups which could be used for chain-lengthening to higher polymers.

Previous work on this project has shown that 1,1,2,8-tetrahydroperfluoro-octene is telomerized by hydrogen peroxide in certain oxygenated solvents to form fluorine-containing telomers bearing hydroxyl and carbonyl groups. These reactions have been investigated further, and the preparation and telomerizations of perfluoroheptene-1 are under investigation. This latter olefin forms telomers of higher fluorine content than the tetrahydroperfluoro-octene.

A reaction of 1,1,2,8-tetrahydroperfluoro-octene in diglyme (diethylene glycol dimethyl ether) at reflux without added free-radical source demonstrated that the peroxides present in the stock diglyme were sufficient to telomerize the olefin to products virtually identical in spectra to previous hydrogen-peroxide-catalyzed reactions. A reaction in peroxide-free diglyme catalyzed by azoisobutyronitrile also afforded very similar material, though in poor yield. These, and previous reactions, confirm the theory that telomerization is initiated through attack of the free-radical source upon the solvent, a fragment of which starts the telomer chain.

A reaction of the fluoro-octene under autogenous pressure at 150°C with 90% hydrogen peroxide in tetrahydrofuran gave very little telomer, in contrast to a published report of reaction of tetrahydrofuran with octene-1 to form 4-dodecanone, an adduct analogous to the telomers of the fluoro-octene. A pressure reaction of the fluoro-octene in tetrahydrofuran initiated by azoisobutyronitrile gave a very small yield of telomer which had nitrile end-groups, but no carbonyl or hydroxyl. This reaction is thus different from previous telomerizations, all of which resulted in incorporation of solvent fragments in the telomers.

Gas chromatographic analysis of the fluoro-octene telomers combined with infrared analysis has proved that the carbonyl and the hydroxyl groups are incorporated into the same telomer molecule and are not physical mixture of the two compound types. The similarity of spectra of the gas-chromatographic fractions also shows that the telomeric product is a mixture of compounds of similar structure, but differing chain length.

After the telomerization of ethylenes bearing a perfluoroalkyl group had been demonstrated to be capable of producing difunctional compounds, the telomerization of still more highly fluorinated olefins was a logical extension. For this work, perfluoroheptene-1 was chosen as the olefin. It was prepared by pyrolysis of sodium perfluoro-octanoate. It was found that a slight excess of base must be used to prevent distillation of the acid during pyrolysis, and that the salt must be dry before pyrolysis to minimize formation of 1-hydroperfluoroheptane. The heptane is difficult to separate from the heptene and may possibly have an adverse effect upon telomer yield.

Telomer yields from perfluoroheptene with 90% hydrogen peroxide have been lower than with the octene, never exceeding 60 percent. The telomers from perfluoroheptene show the same carboxyl, hydroxyl, fluoro and hydrogen functional groups in the infrared as those from the fluoro-octene, but are less viscous and have simpler infrared spectra as would be expected of more completely fluorinated materials. Rather unexpectedly, it has been found

that over 70 percent of these telomers can be steam distilled. The distillate and residue have similar spectra and appear to differ mainly in chain length.

Solvents from which telomers have been produced by refluxing perfluoroheptene with 90% hydrogen peroxide include diglyme, butyl ether, n-butanol, dioxane, and glyme (glycol dimethyl ether). The latter was the only solvent yielding a one-phase reaction mixture at reflux. It, however, neither decreased reaction time nor increased telomer yield as compared with the other solvents.

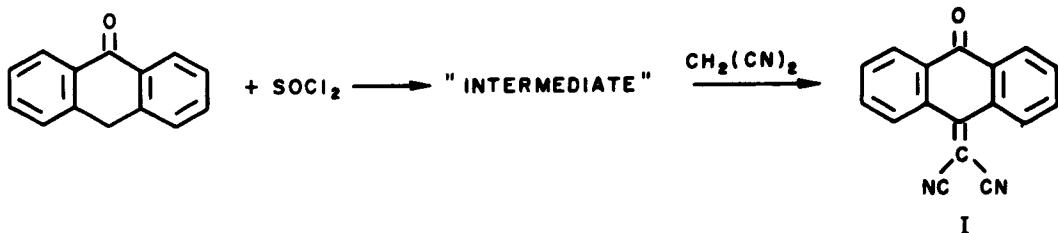
Under autogenous pressure, reactions at 150°C in glyme and diglyme produced similar telomers in similar yields to the refluxed reactions which required a much longer time for complete decomposition of the peroxide. Tetrahydrofuran and a mixture of carbon tetrachloride and diglyme produced virtually no telomer when used as solvents in pressure reactions.

The perfluoroheptene telomers are stable in a 90% solution of boiling hydrogen peroxide. Potassium permanganate partially oxidizes these telomers. Conversion to carboxylic acids bearing very little aliphatic hydrogen is possible by heating with chromium trioxide in acetic acid. Presence of the carboxyl group and near-absence of hydrogen is shown by infrared analysis. Infrared also confirms preparation of the sodium salt of the acids. As in the case of the unoxidized telomers, steam distillation affords a large distillate fraction nearly identical in infrared spectrum to the residue. A portion of the distillate is solid. Part of the solid sublimes to form waxy, rhomboid crystals, which as yet have not been analyzed.

Separation and analysis of homogeneous fractions from the perfluoroheptene telomers and their oxidation products should allow assignment of structures to these materials. Employment of other initiators and solvents should allow differing end-groups to be incorporated into the telomers.

E. REACTIONS OF THIONYL CHLORIDE WITH ANTHRONES AND SUBSTITUTED PHENOLS

In an earlier report (Ref. 5) the discovery of a reaction involving anthrone and thionyl chloride followed by a treatment with malononitrile leading to the synthesis of 10-dicyanomethyleneanthrone (I) in high yield was described.



This reaction is unusual in that I resulted from a union of two active methylene groups to form an ethylenic bond. Although such reactions are not unknown, for example the formation of tetracyanoethylene from malononitrile, it appears that the reactions are quite dissimilar. The reaction encountered here is highly unusual in that, although both anthrone and malononitrile contain extremely reactive methylene groups, the former compound is a tautomer of 9-anthrol. The facile interconversion of anthrone and 9-anthrol would indicate that the reaction path may proceed through either structure. The above reaction gave little or no product when thionyl chloride was replaced by other chlorinating agents, such as sulfonyl chloride, phosphorus trichloride and phosphorus oxychloride. Furthermore, the replacement of malononitrile with other active methylene compounds such as ethyl cyanoacetate, phenylacetonitrile, diphenylmethane and fluorine failed to yield the corresponding substituted methylene anthrone derivatives.

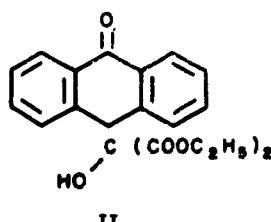
In an effort to study the mechanism of the reaction leading to 10-dicyanomethyleneanthrone, I, the reaction between anthrone and thionyl chloride was investigated. Under two conditions, 10,10'-bianthrone was obtained from the reaction: 1) when thionyl chloride was not used in an excessive amount, and, 2) when attempts were made to isolate the reaction intermediate

by removal of the volatile materials. Upon treatment of the reaction product of anthrone and excess thionyl chloride with crushed ice, an unidentified product was obtained. Attempted purification of this product resulted in its decomposition to anthraquinone. Since 10,10-dichloroanthrone is reported to be stable in ice water under highly acidic conditions and can be recrystallized from aqueous ethanol, it appears reasonable that the dichloroanthrone is not an intermediate in the reaction leading to I.

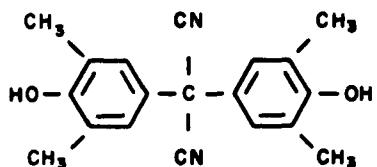
It has been shown that bianthrone, anthraquinone and tetracyanoethylene are not intermediates involved in the synthesis of I. There is also no evidence to indicate that I resulted from the chlorination of malononitrile by thionyl chloride, followed by alkylation of anthrone. Several possible reaction paths for the anthrone-thionyl chloride-malononitrile reaction have been eliminated. There is insufficient evidence at this time to support any specific mechanism. However it is probable that sulfur which contains anthrone intermediates is involved in the mechanism.

In an attempt to prepare a compound similar to I, anthrone was condensed with diethyl ketomalonate (using pyridine as a catalyst) to yield a product identified as 10-(dicarbethoxyhydroxymethyl)anthrone (II).

Attempts were made to dehydrate the product using iodine, p-toluene-sulfonic acid, and sulfuric acid as catalysts and also by refluxing in thionyl chloride; however all attempts failed to yield the desired 10-(dicarbethoxy-methylene)anthrone. The starting material was recovered in each case.

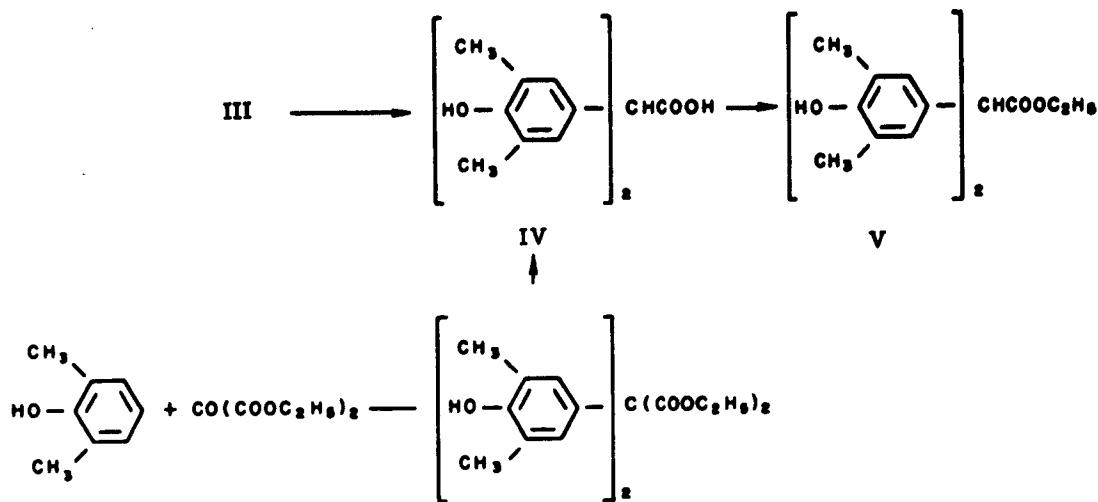


The synthesis of I led to the study of the reaction of 2,6-dimethylphenol, thionyl chloride, and malononitrile. This system is extremely sensitive to reaction conditions, the products being greatly influenced by the reaction temperature, stoichiometry of the reagents, and order of addition. In addition to 4-chloro-2,6-dimethylphenol, the above reaction yielded bis(3,5-dimethyl-4-hydroxyphenyl)malononitrile (III).



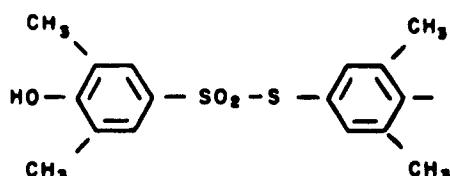
II

The structure of III was determined by hydrolysis and decarboxylation to bis(3,5-dimethyl-4-hydroxyphenyl)acetic acid (IV). This acid was also synthesized by a known independent route (Ref. 6) involving the condensation of 2,6-dimethylphenol and diethyl ketomalonate in cold, concentrated sulfuric acid, followed by hydrolysis and decarboxylation. The two compounds were found to be identical. Esterification of this acid in ethanol yielded the ethyl acetate derivative (V). Acetylation of III with acetic anhydride produced the corresponding diacetate.



Infrared spectra and elemental analyses of the above compounds were in excellent agreement with the proposed structures.

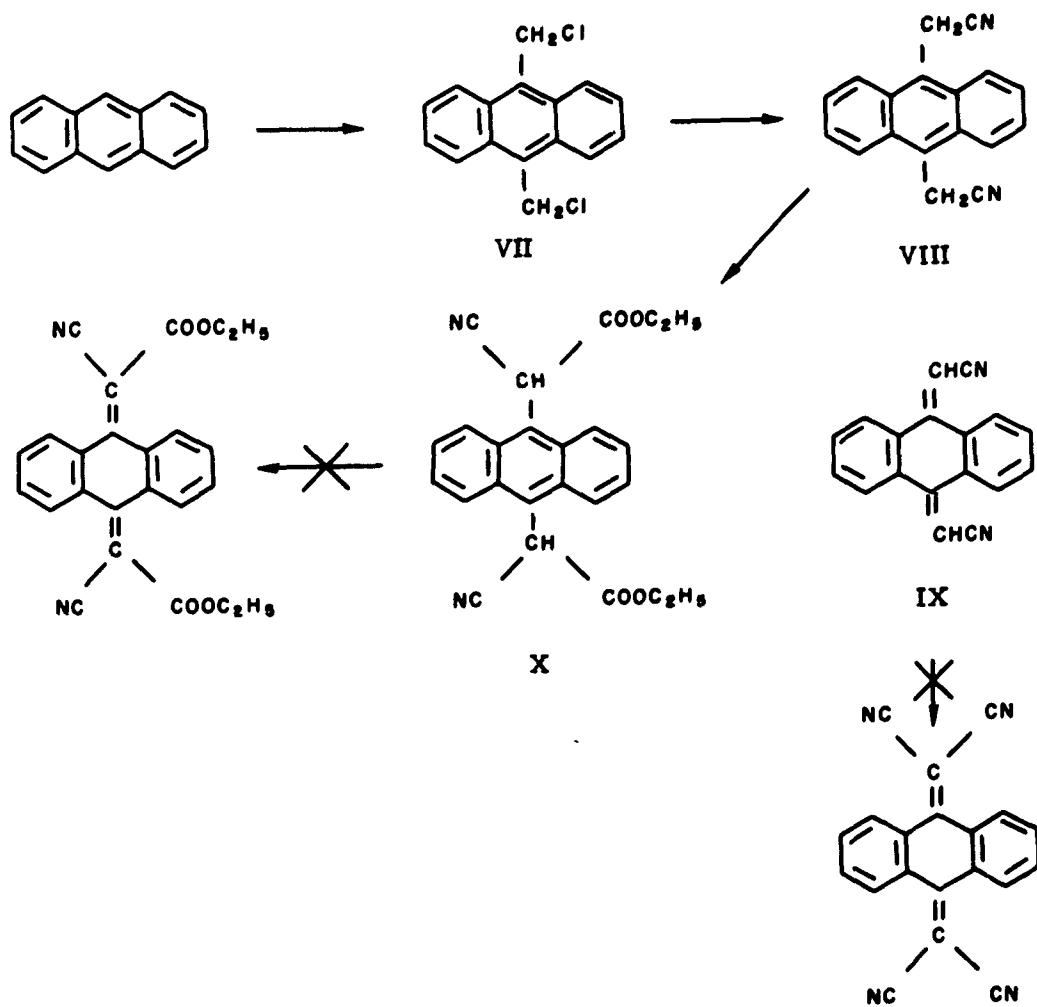
In experiments designed to establish the mechanism of the formation of III, the reaction of 2,6-dimethylphenol and thionyl chloride followed by hydrolysis yielded a product tentatively identified as 3,5-dimethyl-4-hydroxythiophenyl 3,5-dimethyl-4-hydroxybenzenesulfonate (VI).



VI

This thiosulfonate, VI, was readily converted to the corresponding diacetate (VII) with acetic anhydride and pyridine. The infrared spectra and elemental analyses of these two compounds were in agreement with the given structures. Although other isomeric structures may be written, structure VI appears to be the most reasonable. The above thiosulfonate, VI, is the first sulfur-containing compound isolated in this laboratory from the reaction of thionyl chloride and phenolic type compounds. However, it was speculated that sulfur compounds may be possible intermediates in the synthesis of 10-dicyanomethyleneanthrone (I) and bis(3,5-dimethyl-4-hydroxyphenyl)-malononitrile (III). The isolation of this thiosulfonate, VI, would lend validity to a mechanism in the reaction of phenol (including 9-anthrol) and thionyl chloride in which the latter reagent attacks the position para to the hydroxyl group forming an extremely reactive organo-sulfur intermediate. However, further evidence must be obtained before such a mechanism can be proved.

As a possible route to a quinodimethane derivative, anthracene was reacted with formaldehyde and hydrochloric acid to yield 9,10-bis(chloromethyl)-anthracene (VII), Ref. 7. The compound, VII, was converted to the corresponding dinitrile (VIII), also Ref. 7, with potassium cyanide. Treatment of this dinitrile with either sulfonyl chloride or N-bromosuccimide produced 9,10-bis(cyanomethylene)-9,10-dihydroanthracene (IX). Attempted replacement of the cyanomethylene groups, by allowing IX to react with malononitrile, was not successful. Such exchange reactions are reported to proceed readily in certain systems (Ref. 8). Compound VIII was condensed with diethyl carbonate (using potassium t-butoxide as the catalyst) to yield the corresponding bis(cyanocarbethoxymethyl) derivative (X). Attempted oxidation of X with sulfonyl chloride, N-bromosuccimide or bromine did not yield the desired 9,10-bis(cyanocarbethoxymethylene)-9,10-dihydroanthracene.



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PROPELLANT CHEMISTRY INVESTIGATION. SEMIANNUAL TECHNICAL REPORT. Prepared by L. Schieler, Aerodynamics and Propulsion Research Laboratory. 28 February 1963. [28] P. incl. illus. (Report TDR-1693210-10)TR-2, Part I; SSD-TDR-63-34, Part II. (Contract AF 04(695)-169) Unclassified report.

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